SCIENCE FOR CERAMICS PRODUCTION

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PARTICULARITIES OF THE SYNTHESIS OF PIGMENTS WITH CORUNDUM – SPINEL STRUCTURE

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The results of an investigation of the possibility of synthesizing pigments with corundum – spinel structure are presented, and the methods for directed regulation of structure- and phase-formation processes so as to produce pigments with the highest physical – chemical indicators are developed. The relation between the temperature – time parameters of synthesis and the content of modifying oxides and mineralizers with the type and amount of color carrying phases, which give saturated color and a range of pigments colors, are determined.

At the present time ceramic pigments are synthesized on the basis of crystallized compounds which can withstand high temperatures, the dissolving action of glazes and fluxes, and corrosive media. Spinel of the first and second types, corundum, zircon, perovskite, and others, are used as the crystalline acceptor-lattices. When transition metal ions (Cr, Fe, Ni, Co, Mn, and others) are incorporated into the crystal lattice of these minerals, the crystal acquires coloration which is due to the absorption of light because of either $d – d$ transitions of electrons or charge transfer. The ions named above are introduced into the crystal lattice by means of solid-phase reactions, which occur at temperatures 1200 – 1300°C in the presence of mineralizers (H_3BO_3, NaF, and CaF_2).

Isomorphic solid solutions with different compositions are formed when during the synthesis process transition-metal oxides partially or completely substitute for the oxides in the crystalline acceptor-lattices.

The purpose of the present work is to develop methods of directed regulation of the structure and phase formation processes during the synthesis of pigments with corundum – spinel structure which possess a high light reflection coefficient, and high thermal and chemical stability and to determine how the temperature – time parameters of synthesis and the content of the trace modifier-oxide additives and the mineralizers are related with the amount of the color-carrying phases formed, which make it possible to obtain pigments with saturated color and a wide color range.

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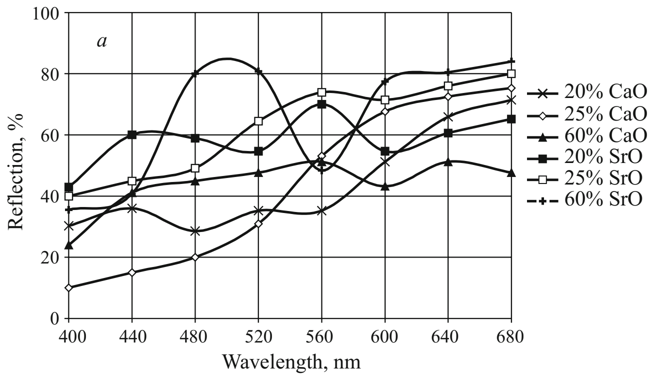
Technical grade alumina (Al_2O_3) was used as the initial component for synthesizing pigments. The following additional components were introduced into the pastes: mineralizer (H_3BO_3), modifiers (ZnO, CaO, CdO, SrO), and chromophore oxides (Cr_2O_3, Fe_2O_3). The powders of the initial components were carefully milled and mixed together. The prepared samples were calcined in an electric furnace at temperature 1100, 1150, and 1200°C with a holding period of 1 h at the maximum temperature.

It was determined that as a result of heat treatment of technical-grade alumina at 1200°C in the presence of a modifier aluminum oxide transforms from the γ into the β form and then into α-Al_2O_3.

Mineralizers have a large effect on the crystal lattice of the synthesized material as well on the color of pigments. The effect of the mineralizers is to form a liquid phase, which loosens the crystal lattice, putting it into an active state. It is known [1] that the reactive power of melt increases sharply when easily polarized components are introduced. In the process, conditions are created for valence bonds of Si^{4+} and Al^{3+} to become saturated as a result of the screening by mobile oxygen ions bond with the easily polarized cations B^{3+} and decreasing the viscosity of the glassy phase. It becomes more mobile and gives rise and promotes not only earlier completion of the phase-formation process but also the appearance of new color-carrying phases. The introduction of mineralizers increases the amount of the color-carrying phases, as a result of which a process resulting in brighter pigments occurs. When a mineralizer is introduced in the



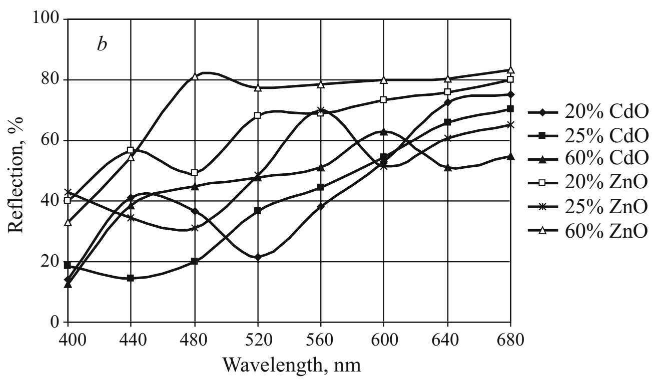


Fig. 1. Spectral-reflection curves of chromium- (*a*) and iron-containing (*b*) pigments with modifiers.

amounts 2.5 – 5.0 wt.% the synthesis temperature of the pigments decreases by 50 – 100°C [2].

Pigments with a wide range of colors were obtained in the system $Al_2O_3 - Cr_2O_3$ depending on the form of the modifier used: light-green, green, yellow, brown, grey, light-blue, and rose colors. The ceramic pigments synthesized in these systems are characterized by a single-tone, bright, and saturated coloration. The pigments fired at lower temperatures have low chromophoric parameters, indicating that the amount of the color-carrying phase in them is too low. Here, it was noted that the samples annealed at higher temperatures (1150°C), have essentially the same chromophoric properties at the samples synthesized at 1100°C.

The color characteristics of the synthesized pigments were determined in the course of the experiments. The dominant wavelength on the spectral-reflection curves lies in the range 500 – 530 nm for the chromium-containing pigments (Fig. 1*a*) and 580 – 590 nm for the iron-containing pigments (Fig. 1*b*).

The pigments which were synthesized using modifiers are characterized by brighter color. This is directly due to their composition and structure. It was determined that pigments with a different range of colors are formed depending on the form of the modifier.

It is known that many ceramic dyes or pigments are spinel-type compounds with the general formula $M^{2+}M_2^{3+}O_4$, where zinc, cadmium, and other metals are divalent metals while aluminum or chromium(iron) substituting for aluminum are trivalent metals. Spinels are mixed oxides; they are coordination polymers, whose crystals consist of tetrahedral $M^{2+}O_4$ and octahedral $M^{3+}O_6$ structural units. Their crystal structure corresponds to cubic face-centered lattice: the O^{2-} ions, occupying the lattice sites, form a close packing [3].

Rose-colored pigments form in the systems $Al_2O_3 - Cr_2O_3 - ZnO$ and $Al_2O_3 - Fe_2O_3 - ZnO$ with the minimum content of Cr^{3+} and Fe^{3+} ions. This is probably due to the fact that the Cr^{3+} and Fe^{3+} ions strive to occupy the positions in tetrahedral vacancies. When the concentration of these ions increases, the color of the pigments changes to green and brown, which is a result of the presence of free oxides Cr_2O_3 and Fe_2O_3 in tetrahedral coordination in the form of the groupings $[CrO_4]$ and $[FeO_4]$ in the paste.

It should be noted that as the content of chromium ions increases, saturation occurs and the tetrahedral vacancies in the spinel are filled, and the chromium ions, having filled the tetrahedra, start to fill octahedra [3]. Since the unit cell parameters change linearly with isomorphic substitutions [4], it can be supposed that the cell parameters increase as the content of the modifier ion increases. Probably, isomorphic substitution of Cr^{3+} ions, whose ionic radius is 0.064 nm, for Al^{3+} ions, whose ionic radius is 0.057 nm, occurs. According to the data in [4], when the ionic radii differ by less than 10%, a series of continuous solid solutions forms. The increase of the lattice parameter is due to the difference in the ionic radii of the chromium and aluminum ions. Here, a chromium ion replaces an aluminum ion not only in octa- but also in tetrahedra.

In the system $Al_2O_3 - Cr_2O_3 - SrO$, light green, mustard, and lemon-yellow colored pigments were formed depending on the amount of the SrO modifier. CaO affects the pigment color similarly. When this oxide is used was a modifier, samples with bright colors with maximum color-tone purity 65% are obtained.

During the synthesis of pigments in the system $Al_2O_3 - Cr_2O_3 - CdO$ it was observed that the color of the samples changed from light-green to turquoise. The purity of the tone of the pigments which are obtained is 55 – 68% and their heat-resistance exceeds 1000°C.

It is well known that the physical – chemical and chromophoric properties of pigments are due to the crystalline phases which are formed. X-ray phase analysis data have established that together with the formation of aluminum-chromium spinels, depending on the modifiers introduced, spinels with the compositions $SrO \cdot Cr_2O_3$, $SrO \cdot Al_2O_3$, $CdO \cdot Al_2O_3$, $ZnO \cdot Al_2O_3$ and $ZnO \cdot Cr_2O_3$, $Fe_2O_3 \cdot Al_2O_3$ as well as the solid solution $(Al, Cr)_2O_3$ are formed. The very small amount of the phase α-Al_2O_3 shows that the spinel formation process is incomplete. When the crystal structure changes, the solid solutions $(Al, Cr)_2O_3$ and $(Al, Fe)_2O_3$ are formed owing to the fact that the ionic radii and the charges of the ions replaced are close. A change of the intensity of the

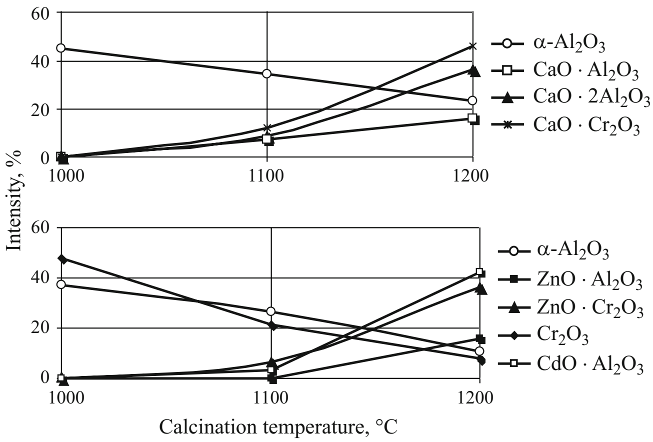


Fig. 2. Variation of the intensity of the diffraction maxima of the crystalline phases of chromium-containing pigments with optimal compositions.

diffraction peaks of the crystal phases formed in chromium- and iron-containing pigments is displayed in Figs. 2 and 3.

The data obtained are confirmed by the results of IR spectroscopy, which attest to the formation of a mixed spinel in the system, since together with the octahedral group $[AlO_6]$ whose bond vibrations manifest at 560 cm^{-1}, characteristic for normal spinels, the absorption bands of the tetrahedral group $[AlO_4]$ at 624.5 cm^{-1}, present in inverted spinels, are also observed. Vibrational frequencies in the range 300 – 450 cm^{-1}, characterizing the range of intense absorption by isolated octahedra $[CrO_6]$, have been recorded in the IR spectra of pigments. Similar results have also been obtained using other modifier oxides. When zinc oxide is used, aluminum-zinc spinels are observed to form. Thus, vibrations of the zinc ion in the tetrahedral coordination $[ZnO_4]$ in the pigments studied were observed at 532.5 and 465.5 cm^{-1}. A decrease of the amount of free Al_2O_3 is observed in the IR spectra of the pigments investigated, which contained modifier oxides in the paste. This is due to spinel formation processes.

The pigments synthesized were tested for chemical resistance. It was established that the values of the chemical resistance depend directly on the phase composition of the pigments, and for the samples obtained they reach 99.1 – 99.2% on average. These pigments possess quite high resistance to chemical reagents (concentrated sulfuric acid, 20% NaOH solution).

The pigments with the compositions proposed above have been approved for use under the conditions of “Keramin” JSC (Republic of Belarus) in the process of volume coloring of ceramic pastes by combining the process of their synthesis and calcination of ceramic granite tiles, which made it possible to decrease the production costs. The pigments proposed are in no way inferior to their imported analogues.

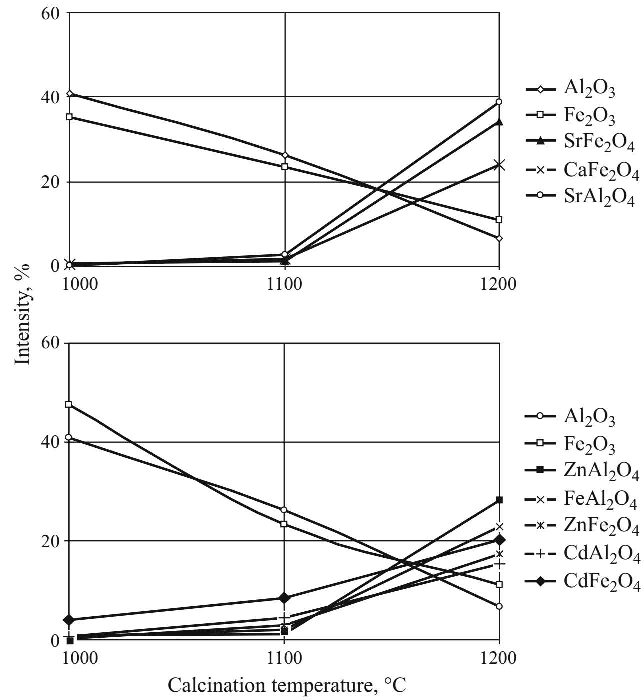


Fig. 3. Variation of the intensity of the diffraction maxima of the crystalline phases of iron-containing pigments with optimal compositions.

The ceramic pigments developed can be recommended for volume coloring of sanitary ware, ceramics tiles, porcelain delftware articles, and glazes; they can also be used successfully as a replacement for imported pigments.

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